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# Preparation and Reactivity of Rhodium and Iridium Complexes Containing a Methylborohydride Based Unit Supported by Two 7-Azaindolyl Heterocycles

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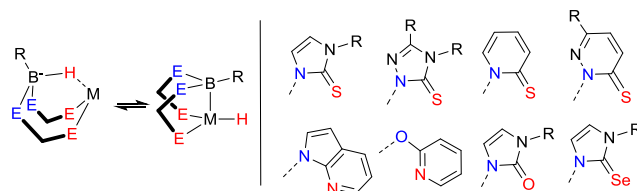
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The synthesis and characterisation of a new anionic flexible scorpionate ligand, methyl(*bis*-7-azaindolyl)borohydride [<sup>Me</sup>Bai]<sup>−</sup> is reported herein. The ligand was coordinated to a series of group nine transition metal centres forming the complexes, [Ir(<sup>Me</sup>Bai)(COD)] (1), [Rh(<sup>Me</sup>Bai)(COD)] (2), [Rh(<sup>Me</sup>Bai)(COD<sup>Me</sup>)] (2-Me) and [Rh(<sup>Me</sup>Bai)(NBD)] (3), where COD = 1,5-cyclooctadiene, COD<sup>Me</sup> = 3-methyl-1,5-cyclooctadiene and NBD = 2,5-norbornadiene. In all cases, the boron based ligand was found to bind to the metal centres *via* a  $\kappa^3$ -N,N,H coordination mode. The ligand and complexes were fully characterised by spectroscopic and analytical methods. The structures of the ligand and three of the complexes were confirmed by X-ray crystallography. The potential for migration of the “hydride” or “methyl” units from boron to the metal centre was also explored. During these studies an unusual transformation, involving the oxidation of the rhodium centre, was observed in complex 2. In this case, the  $\eta^4$ -COD unit transformed into a  $\eta^1, \eta^3$ -C<sub>8</sub>H<sub>12</sub> unit where the ring was bound *via* one sigma bond and one allyl unit. This is the first time such a transformation has been observed at a rhodium centre.

## Introduction

There has been great interest in scorpionate ligands over many years now.<sup>1</sup> Scorpionate ligands are anionic or neutral ligand species that feature a tetrahedral central atom with two or more tethered groups containing donor atoms. One of the many advantages of such ligands is their ability to impart high stability *via* various multidentate coordination modes.<sup>1,2</sup> They are known in many different guises with the central atom being boron-, carbon-, and silicon-based groups to name just a few.<sup>1–3</sup> The wide range of potential tethered groups means that a diverse pool of ligands are already known or are indeed possible. An additional variable relates to the distance between the donor atoms on the tethered group and the central atom. This has a major impact on the resulting chemistry, as exemplified in the case of borohydride-based scorpionates. Original Trofimenko-type scorpionates contain two atoms between the donor atom and the boron centre.<sup>1</sup> The so-called flexible scorpionates, on the other hand contain three atom bridges.<sup>4</sup> The consequences of this means that for the latter ligand type, the borohydride group is typically “pushed” towards the metal centre due to the ring size formed upon chelation to a metal centre (Figure 1, left). In some cases, not

only is the B–H unit close enough to strongly interact with the metal centre, it is also possible to undergo further reactivity leading to the formation of Z-type metal–borane interactions.<sup>5,6</sup> Again, the diversity in potential donor groups of such ligands has already been realised with many examples of both soft and hard donors (Figure 1, right).<sup>4,7–11</sup>



**Fig. 1** – Demonstrating how the B–H group approaches the metal centre as a result of the greater flexibility within the ligand (left). Selected examples highlighting the diversity in tethered groups used within boron based flexible scorpionate ligands (right). E–E = a tethered group containing various donor atoms (right).

With regards to the flexible scorpionate ligands, those based on sulfur are most explored<sup>7</sup> with only limited number of examples based on nitrogen donors<sup>4,8–10</sup> as well as some other donors.<sup>11</sup> To that end, we set out to further explore those ligands based on the 7-azaindole heterocycle. We had previously explored the reactivity of the *tris*-substituted ligand [HB(azaindolyl)<sub>3</sub>]<sup>−</sup> (**Tai**) as well as aryl-substituted versions of the type [ArB(H)(azaindolyl)<sub>2</sub>]<sup>−</sup> (**ArBai**), where Ar = phenyl, mesityl and naphthyl on various transition metal centres (Figure 2).<sup>4,9,10</sup> In some of these cases, the B–H bond in the ligands were found to be activated leading to new transition metal–boron bonds. This appears to be highly dependent on the specific ligand since activation does not occur in all cases despite the remaining components within the coordination sphere of the

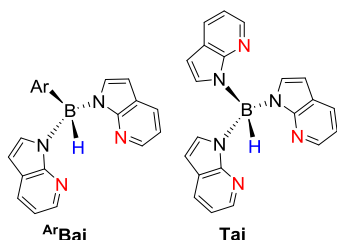
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complexes being identical. It appears that the substituents around the boron centre are important in determining the reactivity of the B–H bond. In order to further understand the requirements for B–H activation, we set out to prepare a new methyl derivative,  $[\text{MeBai}]$ , to explore the impact of changing an aryl group to an alkyl group on the reactivity at the boron centre. We were also interested in whether it would be possible to trigger the migration of the methyl unit in such compounds. Alkyl and aryl migrations from boron to transition metal centre have been observed in a few cases.<sup>12</sup> We prepared this new methyl derivative of  $\text{RBai}$  and a series of complexes in order to explore this potential. The results of our investigation are outlined herein.



**Fig. 2** – The anionic ligands,  $[\text{ArBai}]^-$  and  $[\text{Tai}]^-$  where Ar = phenyl, mesityl and naphthyl.

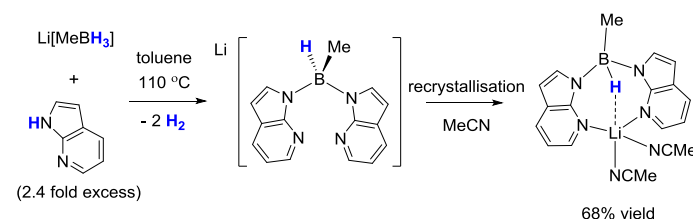
## Results and Discussion

### Synthesis of $\text{Li}[\text{Me}(\text{H})\text{B}(\text{azaindoly})_2]$ , $\text{Li}[\text{MeBai}]$

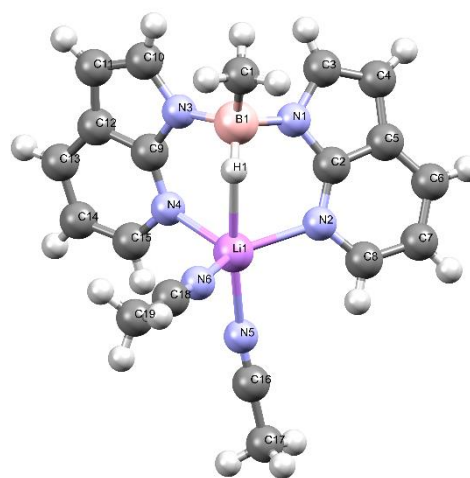
The synthesis of  $\text{Li}[\text{Me}(\text{H})\text{B}(\text{azaindoly})_2]$ ,  $\text{Li}[\text{MeBai}]$ , was achieved from the  $\text{Li}[\text{MeBH}_3]$  precursor (Scheme 1). This was synthesised by the reduction of  $\text{MeB}(\text{OH})_2$  with  $\text{Li}[\text{AlH}_4]$ .<sup>13</sup> To form  $\text{Li}[\text{MeBai}]$ , a 2.4 fold excess of 7-azaindole was added to  $\text{Li}[\text{MeBH}_3]$  in toluene solvent. An immediate reaction was observed as evidenced by the liberation of hydrogen gas from the mixture at room temperature. The reaction was monitored by  $^{11}\text{B}$  NMR spectroscopy. In order to furnish the *bis*-substituted species, it was found that the reaction required heating. Thus, the mixture was heated at 110 °C for a period of 1 h.  $^{11}\text{B}$  NMR spectroscopy confirmed the complete conversion to the target species; one single peak was observed as a doublet at  $-9.7$  ppm ( $^1J_{\text{BH}} = 89$  Hz). The spectroscopically and analytically pure compound was isolated from the reaction mixture in 68% by evaporation of the solvent and recrystallization in acetonitrile. Single crystals, suitable for X-ray diffraction studies were also obtained *via* this method. Details of the structure are provided below.

The salt  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$  was characterised by multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$  and  $^7\text{Li}$  nuclei in  $\text{CD}_3\text{CN}$ ). The spectra were fully consistent with the expected species. The  $^7\text{Li}$  NMR spectrum gave a single peak at 1.62 ppm. The  $^1\text{H}$  NMR spectrum revealed five signals in the aromatic region corresponding to the five proton environments of the 7-azaindoly unit. Each of these signals integrated for 2 protons (10 protons in total) relative to two other signals in the spectrum. The first of these was a relatively broad doublet signal at 0.42 ppm integrating for 3 protons ( $d$ ,  $^3J_{\text{HH}} = 5.3$  Hz)

corresponding to the  $\text{BCH}_3$  group. The second signal was very broad spanning the region between 3.77 and 4.69 ppm (centred at 4.23 ppm). This signal was resolved in the corresponding  $^1\text{H}\{^{11}\text{B}\}$  NMR spectrum and exhibited a clearly resolved quartet splitting pattern with a  $^3J_{\text{HH}}$  coupling of 5.3 Hz. This latter signal integrated for one proton and was therefore consistent with the hydrogen substituent at the boron centre. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$  exhibited seven signals in the aromatic region for the 7-azaindoly heterocycles along with one very broad signal centred at 5.12 ppm, which was difficult to distinguish from the baseline and was only apparent in concentrated samples. This signal was consistent with the methyl carbon bound to the quadrupolar boron centre. Additionally, the assignment for this peak was confirmed by a HSQC experiment which showed its correlation with the doublet for the protons on the methyl substituent.



**Scheme 1** – Synthesis and isolation of  $\text{Li}(\text{MeCN})_2[\text{MeB}(\text{azaindoly})_2]$ ,  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$



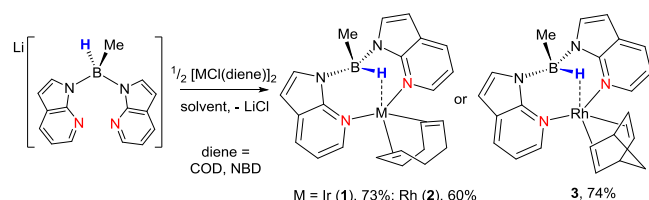
**Fig. 3** – Crystal structure of  $[\text{Li}(\text{MeCN})_2(\kappa^3\text{-N,N,H-MeBai})]$ . Selected bond distances (Å) and angles (°):  $\text{Li}(1)\text{-N}(2)$  2.061(2),  $\text{Li}(1)\text{-N}(4)$  2.074(2),  $\text{Li}(1)\text{-N}(5)$  2.108(2),  $\text{Li}(1)\text{-N}(6)$  2.086(2),  $\text{Li}(1)\text{-H}(1)$  2.168(13),  $\text{B}(1)\text{-H}(1)$  1.148(13),  $\text{B}(1)\text{-C}(1)$  1.6124(16),  $\text{B}(1)\text{-N}(1)$  1.5694(14),  $\text{B}(1)\text{-N}(3)$  1.5627(14),  $\text{N}(1)\text{-B}(1)\text{-N}(3)$  110.63(8),  $\text{N}(2)\text{-Li}(1)\text{-N}(4)$  116.02(10),  $\text{N}(2)\text{-Li}(1)\text{-N}(5)$  98.13(9),  $\text{N}(4)\text{-Li}(1)\text{-N}(5)$  104.75(9),  $\text{N}(6)\text{-Li}(1)\text{-N}(5)$  96.35(9),  $\text{N}(6)\text{-Li}(1)\text{-N}(4)$  109.67(9),  $\text{N}(2)\text{-Li}(1)\text{-N}(6)$  126.14(10).

A sample of the crystals obtained of the ligand were analysed by X-ray crystallography; the resulting structure is shown in Figure 3. It was found that the compound contained two molecules of acetonitrile coordinated to the lithium centre. The molecular structure revealed a mononuclear species involving a lithium centre and one  $\text{MeBai}$  moiety bound to the metal centre *via* a  $\kappa^3\text{-N,N,H}$  coordination mode. The two

coordinated acetonitrile ligands lead to a highly disordered trigonal bipyramidal motif. The N–Li–N angles defining the equatorial plane, consisting of the two azaindoyl donors [N(2) and N(4)] and one acetonitrile molecule [N(6)] are 116.02(10)°, 126.14(10)° and 109.67(9)° [the sum of these angles is 351.83]. The lithium centre is located slightly below the plane defined by these three nitrogen substituents. The B–H unit from the **MeBai** ligand and the second MeCN ligand occupy the axial sites. The boron centre is close to the ideal tetrahedral geometry as expected, the angles involving the non-hydrogen substituents are 110.26(9)°, 110.63(8)° and 110.72(9)°.

The presence of coordinated acetonitrile in the crystalline samples was supported by the infrared spectra of the crystalline samples of  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$  which showed bands typical for coordinated acetonitrile at 2304, 2293 and 2271  $\text{cm}^{-1}$  consistent other examples of a lithium centre containing acetonitrile ligands.<sup>14</sup> An additional band at 2395  $\text{cm}^{-1}$  was also observed which corresponded to the B–H stretch. High resolution mass spectrometry (negative ion ESI) confirmed the presence of the  $[\text{MeBai}]^-$  anion as the most intense peak. Furthermore, the purity of the crystalline  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$  material was confirmed by satisfactory elemental analysis.

With the new ligand precursor in hand, we set out to explore its coordination to some group nine transition metal centres. The complexes,  $[\text{Ir}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{COD})]$  (**1**),  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{COD})]$  (**2**) and  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{NBD})]$  (**3**) were readily synthesised *via* established protocols (Scheme 2).<sup>4</sup> As part of studies, a methyl substituted analogue of complex **2**,  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{COD}^{\text{Me}})]$  (**2-Me**) was also synthesised where 3-methyl-1,5-cyclooctadiene was used in place of the parent diene. The syntheses were carried out in either dichloromethane or tetrahydrofuran solutions containing half an equivalent of the  $[\text{MCl}(\text{diene})]_2$ <sup>15,†</sup> [diene = 2,5-norbornadiene (NBD), 1,5-cyclooctadiene (COD) and 3-methyl-1,5-cyclooctadiene ( $\text{COD}^{\text{Me}}$ )] and a slight excess of  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$ . The chloride was removed from the group nine precursors to form the lithium chloride by-product allowing the borohydride-based ligand to coordinate to the transition metal centres. All complexes were highly soluble in most organic solvents such as diethyl ether, benzene and DCM; they exhibited partial solubility in hexanes. They were therefore isolated from the reaction mixtures *via* evaporation of the reaction solvent, followed by extraction into diethyl ether. Final removal of the diethyl ether gave pure samples of the complexes **1** – **3** as yellow solids in good yields (Scheme 2).



**Scheme 2** – Synthesis of complexes  $[\text{Ir}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{COD})]$  (**1**),  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{COD})]$  (**2**) and  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{NBD})]$  (**3**). The complex,  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{COD}^{\text{Me}})]$  (**2-Me**) was also synthesised *via* an analogous methodology.

Complexes **1** – **3** were fully characterised by spectroscopic and analytical methods. Selected spectroscopic data for these complexes have been provided in Table 1 along with data for previously reported examples. Confirmation of the coordination of the ligand to the metal centre came from their corresponding  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra which revealed a downfield shift of the boron signals from –9.7 ppm to –0.2 ppm for **1**, –5.0 ppm for **2** and –3.6 ppm for **3**. These chemical shifts are consistent with the coordination of the borohydride-based ligands to the iridium and rhodium centres.<sup>4,10</sup> Their corresponding  $^{11}\text{B}$  NMR spectra gave doublet signals at the same chemical shifts with coupling constants 54 Hz (for **1**), 66 Hz (for **2**) and 61 Hz (for **3**). In all three cases there is a reduction in the coupling constants relative to the free ligand (89 Hz) suggesting some degree of interaction of the B–H unit and the group nine metal centres (Table 1). Further information was obtained from the  $^1\text{H}$  NMR spectra of the complexes. In all three cases, a similar pattern with respect to the coordinated azaindoyl units was observed. Broad signals were also observed for the coordinated diene ligands (COD for **1** and **2**, and NBD for **3**). The spectra were consistent with the fact that the two azaindoyl heterocycles, and the two double bonds of the diene, are in the same chemical environment, as expected. Of particular note is the chemical shifts of the  $\text{BCH}_3$  protons which appear approximately 1 ppm of the corresponding signal in the free ligand at 0.42 ppm [*c.f.* 1.30 (**1**), 1.42 (**2**) and 1.35 (**3**)]. The corresponding  $^3J_{\text{HH}}$  values for the  $\text{B}(\text{H})\text{CH}_3$  unit in the complexes are also reduced in comparison to the free ligand which is consistent with a reduction in the  $^1J_{\text{BH}}$  value for the B–H bond upon coordination to the transition metal centres, as a result of a reduction in the B–H bond order. The signals corresponding to the BH hydrogen were only clearly identified in the  $^1\text{H}\{^{11}\text{B}\}$  spectra. In this case, the chemical shifts were found in different regions of the spectrum depending on the metal and diene. The chemical shifts were 2.63 ( $^3J_{\text{HH}} = 3.3$  Hz) for **1**, 6.79 ( $^3J_{\text{HH}} = 4$  Hz) for **2**, 3.26 ( $^3J_{\text{HH}} = 3.1$  Hz) for **3**. As indicated, the  $^3J_{\text{HH}}$  coupling between the methyl hydrogens and the BH was observed in all three cases. In addition to this,  $^1J_{\text{RhH}}$  coupling was apparent for both  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{NBD})]$  and  $[\text{Rh}(\kappa^3\text{-}N,N,H\text{-MeBai})(\text{COD})]$ , where the  $^1J_{\text{RhH}}$  was found to be 13.1 Hz and 4 Hz, respectively.<sup>††</sup> As shown in Table 1,  $^1J_{\text{RhH}}$  is only apparent in four of the eleven rhodium(I) complexes. These coupling constants are a reflection on the nature of the interaction of the B–H unit with the rhodium centre. Currently, we have no clear rationalisation on why  $^1J_{\text{RhH}}$  coupling constants are not observed in all cases.

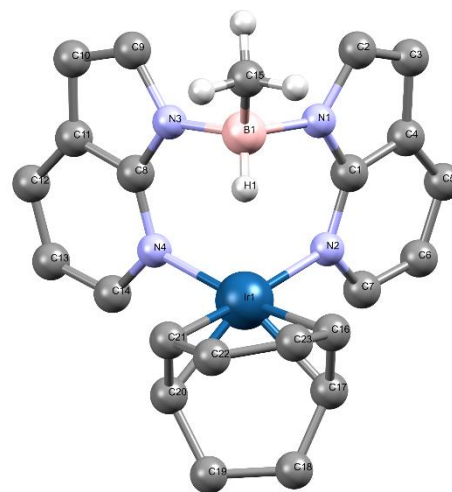
In order to provide further comparison, crystal structures of the three complexes were obtained. Single crystals were readily obtained from saturated hexane or diethyl ether solutions left to stand for periods of 1 – 3 days. The molecular structures of complexes **1**, **2** and **3**, as determined by X-ray crystallography, are shown in Figures 4, 5 and 6, respectively. Selected bond lengths and distances for these three complexes are provided in Table 2. Further details and comparisons with related complexes are provided in the supplementary information in addition to crystallographic parameters for  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$  and complexes **1** – **3**. The molecular structures

of **1** and **3** have one single complex within the asymmetric unit while that of **2** has three independent complexes within the asymmetric unit. The solid state structures of **1** – **3** are consistent with the spectroscopic data discussed above (Table 1) and are thus retained in solution. The structures revealed a  $\kappa^3\text{-N,N,H}$  coordination mode of the **MeBai** ligand to the rhodium(I) and iridium(I) centres. The B–H unit was found to point towards the metal centre while the B–Me unit points away. Two other sites on the metal centres are occupied by the double bonds of the diene ligands (COD for **1** and **2** and NBD for **3**). The geometries about the group nine centres are pseudo square based pyramidal, if each double bond on the diene ligands is considered to occupy one coordination site. The coordination of the **MeBai** ligand within these ligands leads to an eight-membered ring consisting of the two azaindolyl rings bridged by the B(H)Me unit on the pyrrolyl groups and the metal centre at the pyridines. The resulting boat-boat conformation is enforced by the planarity of the azaindolyl rings. This conformation results in the metal centre and the B–H functionality being held in close proximity to each other. The metal-boron distances are thus 2.909(16) Å for **1**, 2.943(3) Å for **2**<sup>5</sup> and 2.9098(18) Å for **3**. These distances are consistent with similar related complexes.<sup>4,10</sup>

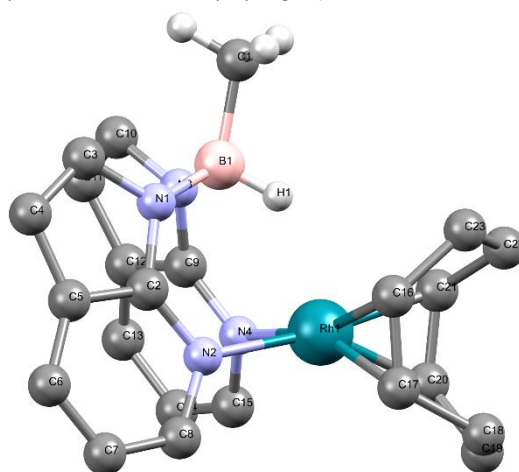
**Table 1** – A comparison of the  $^{11}\text{B}\{^1\text{H}\}$  and  $^1\text{H}\{^{11}\text{B}\}$  NMR and infrared spectroscopic data for complexes **1**, **2**, **2-Me**, **2a** and **3** along with other reported complexes containing 7-azaindolyl based borohydride ligands.

Complex	$^{11}\text{B}\{^1\text{H}\}$ (ppm) <sup>a</sup>	$^{11}\text{B} - ^1\text{J}_{\text{B-H}}$ (Hz)	$^1\text{H}$ BH (ppm) <sup>a</sup>	$^1\text{J}_{\text{RhH}}$ (Hz)	IR (B-H••M) power film (cm <sup>-1</sup> )	Ref
$[\text{Ir}(\text{MeBai})(\text{COD})]$ ( <b>1</b> )	−0.2	54	2.6		1966	
$[\text{Ir}(\text{PhBai})(\text{COD})]$	−0.3	un <sup>d</sup>	3.5 <sup>f</sup>		2004	10c
$[\text{Ir}(\text{MesBai})(\text{COD})]$	−0.8 <sup>b</sup>	un <sup>d</sup>	3.5 <sup>b,f</sup>		2008	10a
$[\text{Ir}(\text{NaphthBai})(\text{COD})]$	−0.7	32	4.2		2037	10a
$[\text{Ir}(\text{Tai})(\text{COD})]$	2.1	59	− <sup>e</sup>		2102	4
$[\text{Rh}(\text{MeBai})(\text{COD})]$ ( <b>2</b> )	−5.0	66	6.8	4 <sup>i</sup>	2157	
$[\text{Rh}(\text{MeBai})(\text{COD}^{\text{Me}})]$ ( <b>2-Me</b> )	−4.9	61	6.8	j	2165	
$[\text{Rh}(\text{MeBai})(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$ ( <b>2a</b> )	−0.8	47	−2.3	24.1	2025	
$[\text{Rh}(\text{PhBai})(\text{COD})]$	−4.6	un <sup>d</sup>	4.2 <sup>f</sup>	j	2117	10c
$[\text{Rh}(\text{MesBai})(\text{COD})]$	−4.9 <sup>b</sup>	un <sup>d</sup>	7.5 <sup>b,f,i</sup>	9.0	2123	10a
$[\text{Rh}(\text{NaphthBai})(\text{COD})]$	−5.4 <sup>c</sup>	60	7.9 <sup>c</sup>	j	2163	10a
$[\text{Rh}(\text{Tai})(\text{COD})]$	−2.2	78	8.3 <sup>f,g,h</sup>	7.2	2106	4
$[\text{Rh}(\text{MeBai})(\text{NBD})]$ ( <b>3</b> )	−3.6	61	3.3	13.1	2075	
$[\text{Rh}(\text{PhBai})(\text{NBD})]$	−3.5	un <sup>d</sup>	4.3	j	2022	10c
$[\text{Rh}(\text{MesBai})(\text{NBD})]$	−4.1 <sup>b</sup>	44	4.2 <sup>b</sup>	j	2064 <sup>h</sup>	10a
$[\text{Rh}(\text{NaphthBai})(\text{NBD})]$	−4.6 <sup>c</sup>	60	4.3 <sup>c</sup>	j	2097	10a
$[\text{Rh}(\text{Tai})(\text{NBD})]$	−1.6 <sup>b</sup> , −1.5 <sup>c</sup>	78	− <sup>e</sup>	j	2015	10c

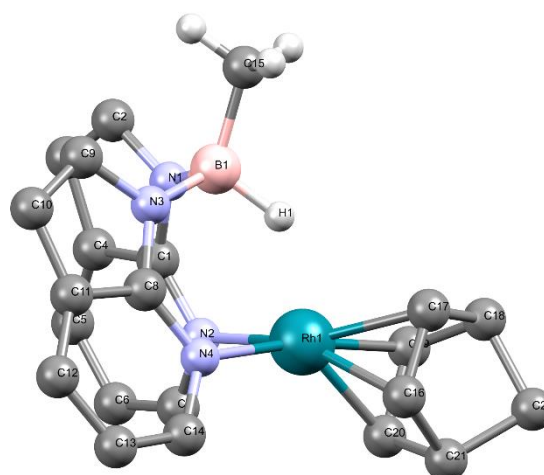
<sup>a</sup> – C<sub>6</sub>D<sub>6</sub> unless otherwise stated, <sup>b</sup> – C<sub>7</sub>D<sub>8</sub>, <sup>c</sup> – CD<sub>2</sub>Cl<sub>2</sub>, <sup>d</sup> – the B–H coupling constant was unresolved due to the broadness of the signal, <sup>e</sup> – not determined, <sup>f</sup> – confirmed by a  $^1\text{H}\{^{11}\text{B}\}$  experiment, <sup>g</sup> – incorrectly provided in reference **4**, <sup>h</sup> – in DCM solvent, <sup>i</sup> – the broadness of this signal meant that the coupling constant could not be measured to a high degree of accuracy, <sup>j</sup> – no  $^1\text{J}_{\text{RhH}}$  coupling was apparent in the spectrum.



**Fig. 4** – Molecular structure of  $[\text{Ir}\{\kappa^3\text{-NNH-MeBai}\}(\text{COD})]$  (**1**) Hydrogen atoms (with the exception of H1 and the methyl hydrogens) have been omitted for clarity.



**Fig. 5** – Molecular structure of  $[\text{Rh}\{\kappa^3\text{-NNH-MeBai}\}(\text{COD})]$  (**2**) Hydrogen atoms (with the exception of H1 and the methyl hydrogens) have been omitted for clarity.

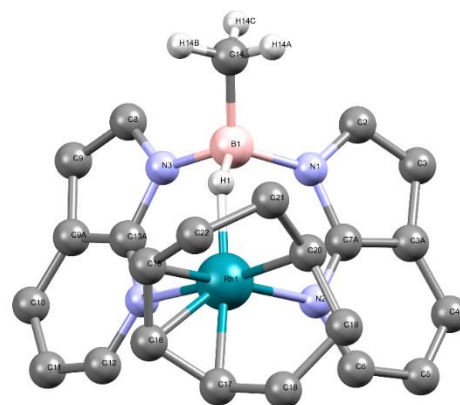


**Fig. 6** – Molecular structure of  $[\text{Rh}\{\kappa^3\text{-NNH-MeBai}\}(\text{NBD})]$  (**3**) Hydrogen atoms (with the exception of H1 and the methyl hydrogens) have been omitted for clarity.

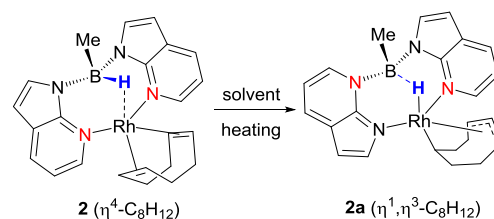


Transformations involving the migration of hydride species from a borohydride unit to transition metal centres and potentially its subsequent insertion into a coordinated organic ligand are now well established.<sup>6c-l</sup> There are also known examples of migration of alkyl and aryl groups from boron, however these are limited in number.<sup>12</sup> The **MeBai** ligand offers two possibilities, either hydride migration or methyl group migration. We therefore attempted to explore this potential reactivity. There was no evidence of any migration in complexes **1** – **3** at room temperature. We set out to find ways in which this reactivity could be triggered by heating the samples. Our initial approach entailed heating solutions of the complexes in a range of solvents. Complexes **1** and **3** showed no indications of reactivity even at elevated temperatures (up to 130 °C) for prolonged periods of time (up to 7 days) across a range of solvents. Complex **2** on the other hand, indeed demonstrated signs of reactivity. A solution of complex **2** in benzene-*d*<sub>6</sub> was heated to 70 °C in a Young's NMR tube and its <sup>11</sup>B NMR spectrum was recorded at regular intervals. The spectrum revealed a new signal at –0.8 ppm, with low intensity, after approximately 1 h corresponding to a new complex **2a**. This downfield shift was somewhat smaller than some of the other “activated complexes” which have undergone hydride migration and the formation of a metal-borane bond (Figure 1, left).<sup>10c</sup> This signal grew very slowly over time. After exhaustive attempts however, we were unable to find conditions to increase the conversion beyond 34%. Other solvents/temperatures used and conversions observed were as follows: hexanes/60 °C (28%); MeCN/80 °C (20%); toluene/100 °C (34%); toluene:THF (5:1)/100 °C (25%); mesitylene/130 °C (21%). Multiple purification steps (see Experimental Section) did lead to samples containing **2a**, which always contained some quantities of **2**. A small sample of single crystals containing pure **2a** was obtained from a saturated hexane solution. The resulting crystal structure (Figure 7) confirmed the identity of complex **2a** as [Rh{κ<sup>3</sup>-*NNH*-**MeBai**}(η<sup>1</sup>,η<sup>3</sup>-C<sub>8</sub>H<sub>12</sub>)] where the COD ligand had been reduced (and the rhodium oxidised) to dianionic species bound to the rhodium centre *via* one σ-bond and one η<sup>3</sup>-coordinated allylic species (Scheme 3).

Complex **2a** was characterised in detail by various NMR experiments. A comparison of its <sup>11</sup>B and <sup>11</sup>B{<sup>1</sup>H} NMR spectra confirmed that the B-H unit was present in the activated species. The signal in the <sup>11</sup>B spectrum exhibited a doublet pattern with a <sup>1</sup>J<sub>BH</sub> coupling constant of 47 Hz which is significantly lower than that in complex **2** (c.f. 66 Hz). Further information was obtained from the corresponding <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra. These confirmed the asymmetry in **2a** where the two “azaindolyl arms” of the **MeBai** ligand are in different chemical environments. The spectra also confirmed the presence of four CH units, now in different chemical environments, on the activated cyclooctenyl species alongside the four CH<sub>2</sub> units. The solution state NMR spectra were therefore fully consistent with the crystal structure obtained for this compound.



**Fig. 7** - Molecular structure of [Rh{κ<sup>3</sup>-*NNH*-**MeBai**}(η<sup>1</sup>,η<sup>3</sup>-C<sub>8</sub>H<sub>12</sub>)] (**2a**) Hydrogen atoms (with the exception of H<sub>1</sub> and the methyl hydrogens) have been omitted for clarity.



**Scheme 3** – The transformation of complex **2** to complex **2a** under thermolytic conditions.

The position of the hydrogen on the BH unit within complex **2a** was of interest. It was located at –2.29 ppm as a broad signal in the standard <sup>1</sup>H NMR experiment and as a doublet (<sup>1</sup>J<sub>RhH</sub> = 24.1 Hz) in the <sup>1</sup>H{<sup>11</sup>B} NMR experiment. The corresponding signal in complex **2** was located at 6.79 ppm. This significant change in the chemical environment and reduction of the <sup>1</sup>J<sub>BH</sub> coupling in the BH unit suggests a stronger interaction between the hydrogen and the rhodium centre (*i.e.* more rhodium-hydride character) in **2a** compared to **2**. This is also reflected in a difference in the B-H••Rh stretching frequencies for IR spectrum, which revealed a bands at 2157 cm<sup>–1</sup>, for **2**, and 2025 cm<sup>–1</sup> for **2a**. Both of these observations are consistent with an increase in the oxidation state from Rh(I) in **2** to Rh(III) in **2a**.<sup>10a,d,16</sup> There were no significant changes to the coordination of the **MeBai** ligand between **2** and **2a** (see Table 2). The bond distances and angles were similar. The only clear difference was the reduction of the Rh–B distances. For complex **2**, the distances in the three complex within the asymmetric unit were found in the range 2.943(3) Å to 2.957(3) Å, whilst the corresponding distances in **2a** were 2.733(4) Å and 2.736(4) Å, respectively. This observation again reflects the increased oxidation state in **2a**. The transformation of 1,5-COD to the η<sup>1</sup>,η<sup>3</sup>-C<sub>8</sub>H<sub>12</sub> unit has previously been observed in many cases at iridium centres.<sup>17</sup> There is also one example of such a transformation within a cobalt complex.<sup>18</sup> To the best of our knowledge, the transformation of 1,5-COD to the η<sup>1</sup>,η<sup>3</sup>-C<sub>8</sub>H<sub>12</sub> has not been previously reported at a rhodium centre. This is

with the exception of one example where an external oxidant ( $\text{H}_2\text{O}_2$  or  $\text{O}_2$  in the presence of an acid) and an oxygen atom is incorporated into the ring.<sup>19</sup> Given the prevalence of the transformation of COD at iridium centres, it is surprising that complex **1** does not undergo the same rearrangement that **2** does. From the previously reported iridium examples, it appears that there is a requirement for the generation of an iridium–hydride intermediate. We are therefore carrying out further investigations with these systems to explore whether there is a boron-to-rhodium hydride migration step involved in the transformation of complex **2** to complex **2a**. We are also investigating methodologies to increase the rate of transformation and percentage conversions to this product.

## Experimental

### General Remarks

All manipulations were carried out using standard Schlenk techniques. Solvents were supplied extra dry from Acros

Organics and were stored over 4 Å molecular sieves.  $\text{CD}_3\text{CN}$  and  $\text{C}_6\text{D}_6$  NMR solvents were stored in a Young's ampules under  $\text{N}_2$ , over 4 Å molecular sieves and were degassed through three freeze-thaw cycles prior to use. All reagents were used as purchased from commercial sources. The complexes  $[\text{Ir}(\text{COD})\text{Cl}]_2$ ,<sup>15a</sup>  $[\text{Rh}(\text{COD})\text{Cl}]_2$ ,<sup>15b</sup>  $[\text{Rh}(\text{COE})\text{Cl}]_2$ ,<sup>15c</sup> and  $[\text{Rh}(\text{NBD})\text{Cl}]_2$ ,<sup>15d</sup> were synthesised according to standard literature procedures. NMR experiments were conducted on Bruker 400 MHz Ascend™ 400, JEOL ECP300, Varian VNMR S500 or JEOL ECP400 spectrometers. Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) assignments (Figure 8) were supported by HSQC, HMBC and COSY NMR experiments. Infrared spectra were recorded on Perkin-Elmer Spectrum Two and Spectrum 100 ATR FT-IR spectrometers. Mass spectra were recorded by the EPSRC NMSF at Swansea University or on a VG Analytic Quattro in ESI<sup>+</sup> or EI<sup>+</sup> mode. Elemental analysis was performed at London Metropolitan University by their elemental analysis service or the microanalytical laboratory of the School of Chemistry at the University of Bristol. The borohydride,  $\text{Li}[\text{CH}_3\text{BH}_3]$  was prepared according to a literature procedure.<sup>13</sup>

Table 2 – Selected bonding distances (Å) and angles (°) for complexes **1**, **2**, **2a** and **3**.

	Complex 1	Complex 2 <sup>c</sup>	Complex 2a <sup>d</sup>	Complex 3
	$[\text{Ir}(\text{MeBai})(\text{COD})]$	$[\text{Rh}(\text{MeBai})(\text{COD})]$	$[\text{Rh}(\text{MeBai})(\eta^1, \eta^3\text{-C}_8\text{H}_{12})]$	$[\text{Rh}(\text{MeBai})(\text{NBD})]$
M–N <sup>a</sup>	2.137(11)	2.136(2) / 2.1455(19) / 2.1416(19)	2.219(3) / 2.227(3)	2.2054(13)
M–N <sup>b</sup>	2.134(10)	2.134(2) / 2.1324(19) / 2.130(2)	2.110(3) / 2.100(3)	2.1139(13)
M–B	2.909(16)	2.943(3) / 2.944(3) / 2.957(3)	2.736(4) / 2.733(4)	2.9098(18)
B–N <sup>a</sup>	1.568(18)	1.557(3) / 1.559(3) / 1.565(3)	1.550(6) / 1.551(6)	1.559(2)
B–N <sup>b</sup>	1.548(18)	1.565(3) / 1.561(3) / 1.559(3)	1.538(6) / 1.538(6)	1.558(2)
B–C	1.603(19)	1.601(3) / 1.601(3) / 1.603(3)	1.608(6) / 1.607(6)	1.606(2)
N–M–N	87.4(4)	87.17(8) / 87.77(7) / 87.32(7)	88.10(12) / 87.72(12)	90.12(5)
N–B–N	109.6(10)	107.51(18) / 108.75(18) / 108.45(18)	112.2(3) / 111.1(3)	107.35(12)
N <sup>a</sup> –B–C	111.8(11)	112.7(2) / 112.37(19) / 111.73(19)	112.4(4) / 112.9(3)	111.43(12)
N <sup>b</sup> –B–C	113.5(12)	112.65(19) / 112.33(19) / 112.25(19)	112.0(3) / 111.8(3)	113.35(13)
Σ of angles of non-hydrogen substituents at boron	334.9	332.9 / 333.5 / 332.4	336.6/335.8	332.1
M–B–C	136.4(10)	138.62(17) / 138.15(16) / 139.84(15)	131.8(3) / 131.6(3)	137.99(11)

<sup>a</sup> – the values corresponding to the heterocyclic unit which has the longest M–N distance within structure, <sup>b</sup> – the values corresponding to the heterocyclic unit which has the shortest M–N distance within structure, <sup>c</sup> – three independent molecules in the unit cell, <sup>d</sup> – two independent molecules in the unit cell.

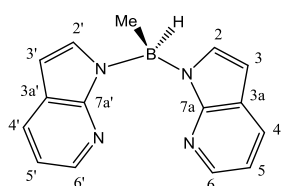


Fig. 8 – Numbering scheme for the assignments of the azaindolyl unit within the ligand and complexes. The azaindolyl rings are in the same chemical environment in all complexes apart from complex **2a**.

### Synthetic Procedures

#### Synthesis of $\text{Li}(\text{MeCN})_2[\text{B}(\text{Me})\text{H}(\text{azaindolyl})_2]$ , $\text{Li}(\text{MeCN})_2[\text{MeBai}]$

A Schlenk flask was charged with  $\text{Li}[\text{MeBH}_3] \cdot 0.8 \text{ THF}$  (892 mg, 9.53 mmol) and toluene (25 mL, 0.4 M). Azaindole (2.720 g,

23.02 mmol, 2.4 equiv.) was added in portions under a nitrogen atmosphere leading to hydrogen evolution. The clear mixture was further stirred until no more hydrogen gas was observed. The system was carefully placed under partial vacuum and heated at 110 °C for 1 h (**care**: an overpressure will be generated). After this time, the solution was separated by filtration and all volatiles removed by vacuum to give a white powder. This was recrystallised from a concentrated acetonitrile solution to give the product as colourless crystalline solid (combined from three crystallisation crops). Yield: 2.261 g, 6.46 mmol, 68%.  $^1\text{H}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): 8.25 [2H, dd,  $^3J_{\text{HH}} = 4.92 \text{ Hz}$ ,  $^4J_{\text{HH}} = 1.65 \text{ Hz}$ , aza-CH(6)], 7.85 [2H, dd,  $^3J_{\text{HH}} = 7.70 \text{ Hz}$ ,  $^4J_{\text{HH}} = 1.65 \text{ Hz}$ , aza-CH(4)], 7.66 [2H, d,  $^3J_{\text{HH}} = 3.28$ , aza-CH(2)], 6.91 [2H, dd,  $^3J_{\text{HH}} = 7.70 \text{ Hz}$ ,  $^3J_{\text{HH}} = 4.95 \text{ Hz}$ , aza-CH(5)], 6.32 [2H, d,  $^3J_{\text{HH}} = 3.28 \text{ Hz}$ , aza-CH(3)], 4.69 – 3.77 (1H, v. br. m, BH), 0.42 [3H, d,  $^1J_{\text{BH}} = 5.32 \text{ Hz}$ ,  $\text{BCH}_3$ ].  $^1\text{H}\{^{11}\text{B}\}$  NMR, partial,  $\delta$  ( $\text{CD}_3\text{CN}$ ): 4.23 [1H, q,  $^1J_{\text{BH}} = 5.32 \text{ Hz}$ , BH].  $^{11}\text{B}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ): –9.72 (d,  $^1J_{\text{BH}} = 88.86 \text{ Hz}$ , BH).

$^{11}\text{B}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ):  $-9.72$  (s, h.h.w. =  $72.5$  Hz).  $^7\text{Li}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ):  $1.62$  (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CD}_3\text{CN}$ ):  $152.01$  [aza-C(7a)],  $141.54$  [aza-CH(6)],  $132.32$  [aza-CH(2)],  $129.40$  [aza-CH(4)],  $123.90$  [aza-C(3a)],  $114.36$  [aza-CH(5)],  $99.45$  [aza-CH(3)],  $5.16$  [ $\text{BCH}_3$ , observed indirectly from HSQC experiment]; Elem. Anal.: Calcd for  $\text{C}_{19}\text{H}_{20}\text{BLiN}_6 \cdot \{\text{Li}[\text{MeBai}]\cdot 2\text{CH}_3\text{CN}\}$ : C 65.17; H 5.76; N 24.00; Found: C 65.11; H 5.63; N 23.51. HRMS (ESI/LTQ Orbitrap XL)  $m/z$ :  $[\text{M}]^-$  Calcd for  $\text{C}_{15}\text{H}_{14}\text{BN}^-$  261.1317; Found 261.1315. IR (powder film):  $2395\text{ cm}^{-1}$  ( $\nu_{\text{BH}}$ ),  $2304$  ( $\nu_{\text{C}\equiv\text{N}}$ ),  $2293$  ( $\nu_{\text{C}\equiv\text{N}}$ ) and  $2271$  ( $\nu_{\text{C}\equiv\text{N}}$ )  $\text{cm}^{-1}$  (band attributable to stretching frequencies for coordinated acetonitrile).

### Synthesis of $[\text{Ir}\{\kappa^3\text{-}N,N,H\text{-B(Me)H(azaindoly)}\}_2\{\text{COD}\}]$ (1)

A Schlenk flask was charged with  $[\text{IrCl}(\text{COD})]_2$  (100.7 mg, 0.15 mmol) and the ligand,  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$  (104.9 mg, 0.30 mmol, 2 equiv.). Dry/degaussed THF (15 mL) was added at room temperature under a nitrogen atmosphere to give a yellow solution. The mixture was stirred for 4 h at room temperature and all volatiles were removed by oil pump vacuum. The residue was extracted with dry diethyl ether ( $2 \times 20$  mL) and filtered *via* cannula into a Schlenk flask. The solvent volume was removed by vacuum to give the crude product as a yellow solid, 123.0 mg, 2.20 mmol, 73%. Yellow single crystals were grown from a concentrated diethyl ether solution upon standing at room temperature for 72 h.  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $8.54$  [2H, dd,  $^3J_{\text{HH}} = 5.54$ ,  $^4J_{\text{HH}} = 1.48$  Hz, aza-CH(6)],  $7.53$  [2H, d,  $^3J_{\text{HH}} = 3.31$  Hz, aza-CH(2)],  $7.25$  [2H, dd,  $^3J_{\text{HH}} = 7.70$  Hz,  $^4J_{\text{HH}} = 1.54$  Hz, aza-CH(4)],  $6.39$  [2H, d,  $^3J_{\text{HH}} = 3.33$  Hz aza-CH(3)],  $6.32$  [2H, dd,  $^3J_{\text{HH}} = 7.69$  Hz,  $^3J_{\text{HH}} = 5.54$  Hz aza-CH(5)],  $3.46 - 3.36$  (4H, br m, CH=CH, COD),  $2.94 - 2.37$  (1H, overlapping br m, BH),  $2.45 - 2.31$  (4H, overlapping br m,  $\text{CH}_2$ , COD),  $1.71 - 1.54$  (4H, br m,  $\text{CH}_2$ , COD),  $1.31$  (3H, d,  $^2J_{\text{BH}} = 2.80$  Hz,  $\text{BCH}_3$ ).  $^1\text{H}\{^{11}\text{B}\}$  NMR, partial,  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $2.63$  (1H, br q,  $^1J_{\text{BH}} = 3.26$  Hz, BH).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $153.80$  [aza-C(7a)],  $143.67$  [aza-C(6)],  $130.48$  [aza-C(2)],  $128.76$  [aza-C(4)],  $124.57$  [aza-C(3a)],  $114.81$  [aza-C(5)],  $102.06$  [aza-C(3)],  $57.39$  (br s, CH=CH, COD),  $32.91$  ( $\text{CH}_2$ , COD),  $3.91$  [br m, B- $\text{CH}_3$  observed indirectly from HSQC].  $^{11}\text{B}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-0.23$  (d,  $^1J_{\text{BH}} = 54.44$  Hz).  $^{11}\text{B}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-0.23$  (s, hhw =  $72$  Hz); HRMS (ASAP+/TOF MS)  $m/z$ :  $[\text{M-H}]^+$  Calc. for  $\text{C}_{23}\text{H}_{25}\text{BIRN}_4$  559.1782. Found: 559.1776. IR (powder film):  $1966\text{ cm}^{-1}$  ( $\nu_{\text{BH}}$ ). Elem. Anal.: Calcd for  $\text{C}_{23}\text{H}_{26}\text{BIRN}_6 \cdot 0.2$  pentane: C 50.26; H 5.04; N 9.67; Found: C: 50.22; H 4.78; N 9.71.

### Synthesis of $[\text{Rh}\{\kappa^3\text{-}N,N,H\text{-B(Me)H(azaindoly)}\}_2\{\text{COD}\}]$ (2)

A Schlenk flask was charged with  $[\text{RhCl}(\text{COD})]_2$  (50.2.7 mg, 0.10 mmol) and 90.6 mg (0.25 mmol, 2.5 equiv.) of the ligand,  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$ . Dry/degaussed THF (5.0 mL) was added by syringe under a nitrogen atmosphere to give a yellow solution. The mixture was stirred for 1 h at room temperature and all volatiles were removed by oil pump vacuum. The residue was extracted with dry diethyl ether ( $2 \times 20$  mL) and filtered into a Schlenk flask *via* cannula. The solvent volume was reduced to a minimum to give 57.9 mg, 0.12 mmol, 60% of a yellow crystalline solid which was recrystallized from a concentrated diethyl ether solution and dried under vacuum for several hours.  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $8.51$  [2H, d,  $^3J_{\text{HH}} = 5.29$  Hz, aza-CH(6)],

$7.71$  [2H, d,  $^3J_{\text{HH}} = 3.30$  Hz, aza-CH(2)],  $7.27$  [2H, dd,  $^3J_{\text{HH}} = 7.66$  Hz,  $^4J_{\text{HH}} = 1.27$  Hz, aza-CH(4)],  $6.79$  (1H, br d  $^1J_{\text{BH}} = 85$  Hz, BH),  $6.39$  (2H, dd,  $^3J_{\text{HH}} = 7.66$  Hz,  $^3J_{\text{HH}} = 5.46$  Hz, aza-CH(5));  $6.27$  [2H, d,  $^3J_{\text{HH}} = 3.28$  Hz, aza-CH(3)],  $3.72 - 3.60$  [4H, br m, CH=CH, COD],  $2.55 - 2.37$  [4H, br m,  $\text{CH}_2$ , COD],  $1.54 - 1.72$  [4H, m,  $\text{CH}_2$ , COD],  $1.41$  [3H, d,  $^2J_{\text{BH}} = 4.01$  Hz,  $\text{BCH}_3$ ].  $^1\text{H}\{^{11}\text{B}\}$  NMR, partial,  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $6.79$  (1H, dq, apparent coupling  $^3J_{\text{HH}} = 4$  Hz,  $^1J_{\text{RHH}} = 8$  Hz, BH).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $152.39$  [aza-C(7a)],  $143.24$  [aza-C(6)],  $131.59$  [aza-C(2)],  $128.56$  [aza-C(4)],  $124.82$  [aza-C(3a)],  $114.24$  [aza-C(5)],  $100.82$  [aza-C(3)],  $76.06$  [br m, CH=CH, COD],  $31.60$  [ $\text{CH}_2$ , COD],  $3.66$  [br m B- $\text{CH}_3$  observed indirectly from HSQC].  $^{11}\text{B}$ -NMR (96.2 MHz)  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-4.99$  (d,  $^1J_{\text{B-H}} = 65.69$  Hz, BH);  $^{11}\text{B}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $-4.99$  (s, hhw =  $82$  Hz). HRMS (ASAP+/TOF MS)  $m/z$ :  $[\text{M-H}]^+$  Calc. for  $\text{C}_{23}\text{H}_{25}\text{BN}_4\text{Rh}$  471.1231. Found: 471.1233. IR (powder film):  $2157\text{ cm}^{-1}$  ( $\nu_{\text{BH}}$ ). Elem. Anal.: Calcd for  $\text{C}_{23}\text{H}_{26}\text{BN}_4\text{Rh}$ : C 58.50; H 5.55; N 11.87; Found: C: 58.58; H 5.65; N 11.65.

### Synthesis of $[\text{RhCl}(\text{COD}^{\text{Me}})]_2$

A Schlenk flask was charged with  $[\text{RhCl}(\text{COE})_2]_2$  (102.1 mg, 0.14 mmol) and dry/degaussed THF (4 mL) was added to give an orange solution. Addition of  $\text{COD}^{\text{Me}}$  (45  $\mu\text{L}$ , 0.32 mmol, 2.3 equiv.) gave a yellow solution which was further stirred for 1 h. The solvent was removed by vacuum and the residue redissolved in absolute EtOH (5 mL). The solution was kept in a fridge overnight to give the expected product as orange crystals (65 mg, 0.12 mmol, 86%).  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ):  $4.28 - 4.16$  [4H, m, CH=CH,  $\text{COD}^{\text{Me}}$ ],  $2.65 - 2.53$  [1H, m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $2.50 - 2.35$  [1H, m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $2.29 - 2.17$  [1H, br m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $2.08 - 1.98$  [1H, br overlapping m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $2.04$  [1H, overlapping br m, CH,  $\text{COD}^{\text{Me}}$ ],  $1.91 - 1.80$  [1H, br m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $1.74 - 1.62$  [1H, br m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $1.47$  [3H, d,  $^3J_{\text{HH}} = 6.07$  Hz,  $\text{CH}_3$ ,  $\text{COD}^{\text{Me}}$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  ( $\text{CDCl}_3$ ):  $76.35$  [overlapping m, CH=CH,  $\text{COD}^{\text{Me}}$ ],  $40.51$  [ $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $37.08$  [CH,  $\text{COD}^{\text{Me}}$ ],  $31.72$  [ $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $30.51$  [ $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $23.71$  [ $\text{CH}_3$ ,  $\text{COD}^{\text{Me}}$ ]. IR (powder film):  $1452\text{ cm}^{-1}$  ( $\nu_{\text{CH=CH}}$ ).

### Synthesis of $[\text{Rh}\{\kappa^3\text{-}N,N,H\text{-B(Me)H(azaindoly)}\}_2\{\text{COD}^{\text{Me}}\}]$ (2-Me)

A Schlenk flask was charged with  $[\text{RhCl}(\text{COD}^{\text{Me}})]_2$  (30.1 mg, 0.06 mmol) and the ligand,  $\text{Li}(\text{MeCN})_2[\text{MeBai}]$  (42.4 mg, 0.12 mmol, 2.1 equiv.) under a nitrogen atmosphere. Dry/degaussed benzene (0.8 mL) was added and the mixture stirred for 1h. The solvent was removed, the residue extracted with pentane ( $3 \times 5$  mL) and filtered *via* cannula into a Schlenk flask. The solvent was reduced to a 2 mL and the solution was kept at  $4^\circ\text{C}$  overnight to give the product as a yellow powder (33 mg, 0.07 mmol, 59%).  $^1\text{H}$  NMR  $\delta$  ( $\text{C}_6\text{D}_6$ ):  $8.59$  [1H, d,  $^3J_{\text{HH}} = 5.20$  Hz, aza-CH(6)],  $8.56$  [1H, d,  $^3J_{\text{HH}} = 5.29$  Hz, aza-CH(6')],  $7.71$  [2H, d,  $^3J_{\text{HH}} = 3.21$  Hz, aza-CH(2)],  $7.28$  [1H, dd,  $^3J_{\text{HH}} = 7.56$  Hz,  $^4J_{\text{HH}} = 1.29$  Hz, aza-CH(4)],  $7.26$  [1H, dd,  $^3J_{\text{HH}} = 7.51$  Hz,  $^4J_{\text{HH}} = 1.29$  Hz, aza-CH(4')],  $6.42$  [1H, dd,  $^3J_{\text{HH}} = 7.65$  Hz,  $^3J_{\text{HH}} = 5.44$  Hz, aza-CH(5)],  $6.39$  [1H, dd,  $^3J_{\text{HH}} = 7.65$  Hz,  $^3J_{\text{HH}} = 5.44$  Hz, aza-CH(5')],  $6.27$  [1H, d,  $^3J_{\text{HH}} = 3.23$  Hz aza-CH(3)]  $6.26$  [1H, d,  $^3J_{\text{HH}} = 3.26$  Hz aza-CH(3')],  $3.70 - 3.58$  (2H, br m, =CH,  $\text{COD}^{\text{Me}}$ ),  $3.57 - 3.50$  [1H, br m, =CH,  $\text{COD}^{\text{Me}}$ ],  $3.38 - 3.32$  [1H, br m, =CH,  $\text{COD}^{\text{Me}}$ ],  $2.56 - 2.39$  [2H, m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $2.13 - 2.04$  [1H, m,  $\text{CH}_2$ ,  $\text{COD}^{\text{Me}}$ ],  $2.02 - 1.93$  [1H, m, CH,



$COD^{Me}$ ], 1.86 – 1.77 [1H, m,  $CH_2$ ,  $COD^{Me}$ ], 1.72 – 1.53 [2H, m,  $CH_2$ ,  $COD^{Me}$ ], 1.45 [3H, d, 6.77 Hz,  $COD^{Me}$ ], 1.42 [1H, d, 3.97 Hz,  $BCH_3$ ].  $^1H\{^{11}B\}$  NMR, partial,  $\delta$  ( $C_6D_6$ ): 6.86 (1H, br m, BH).  $^{13}C\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): 152.46 [aza-C(7a')], 152.39 [aza-C(7a)], 143.41 [aza-C(6')], 143.16 [aza-C(6)], 131.63 [aza-C(2)], 131.58 [aza-C(2')], 128.58 [overlapped signal for aza-C(4) and aza-C(4')], 124.85 [aza-C(3a')], 124.83 [aza-C(3a)], 114.29 [aza-C(5')], 114.24 [aza-C(5)], 100.87 [aza-C(3')], 100.84 [aza-C(3)], 82.18 [br m,  $CH=CH$ ,  $COD^{Me}$ ], 76.33 [br m,  $CH=CH$ ,  $COD^{Me}$ ], 74.95 [br m,  $CH=CH$ ,  $COD^{Me}$ ], 73.25 [br m,  $CH=CH$ ,  $COD^{Me}$ ], 39.94 [ $CH_2$ ,  $COD^{Me}$ ], 37.80 [ $CH$ ,  $COD^{Me}$ ], 31.60 [ $CH_2$ ,  $COD^{Me}$ ], 30.89 [ $CH_2$ ,  $COD^{Me}$ ], 24.12 [ $CH_3$ ,  $COD^{Me}$ ], 3.85 [br m, B- $CH_3$  observed indirectly from HSQC].  $^{11}B$ -NMR (96.2 MHz)  $\delta$  ( $C_6D_6$ ): -4.90 (d,  $^1J_{B-H}$  = 61.13 Hz, BH);  $^{11}B\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): -4.99 (s, hhw = 91 Hz). IR (powder film): 2165  $cm^{-1}$  ( $\nu_{BH}$ ).

### Synthesis of $[Rh\{\kappa^3-N,N,H-B(Me)H(azaindoly)l_2\}(NBD)]$ (**3**)

A Schlenk flask was charged with  $[RhCl(NBD)]_2$  (100.7 mg, 0.22 mmol) and the ligand  $Li(MeCN)_2[MeBai]$  (152.7 mg, 0.44 mmol, 2.0 equiv.). Dry/degassed THF (10 mL) was added under a nitrogen atmosphere to give a yellow solution. The mixture was stirred for 1 h at room temperature and all volatiles were removed by oil pump vacuum. The residue was extracted with dry diethyl ether (3  $\times$  10 mL) and filtered *via* cannula into a Schlenk flask. The solvent volume was removed by oil pump vacuum to give the product as a yellow solid (148.0 mg, 0.32 mmol, 74%). Yellow single crystals were grown from a concentrated diethyl ether solution upon standing at room temperature for 24 h.  $^1H$  NMR  $\delta$  ( $C_6D_6$ ): 8.27 [2H, d,  $^3J_{HH}$  = 5.25 Hz, aza-CH(6)], 7.64 [2H, d,  $^3J_{HH}$  = 3.32 Hz, aza-CH(2)], 7.35 [2H, dd,  $^3J_{HH}$  = 7.64 Hz,  $^4J_{HH}$  = 1.14 Hz, aza-CH(4)], 6.46 [2H, dd,  $^3J_{HH}$  = 7.64 Hz,  $^3J_{HH}$  = 5.38 Hz, aza-CH(5)], 6.32 [2H, d,  $^3J_{HH}$  = 3.30 Hz aza-CH(3)], 3.44 – 3.37 (2H, br m,  $CH_2$ , NBD), 3.26 (1H, m, BH), 3.19 – 3.12 (4H, m,  $CH=CH$ , NBD), 1.35 (3H, d,  $^2J_{B-Me}$  = 3.49 Hz), 0.94 (2H, virtual t,  $^3J_{HH}$  = 1.6 Hz,  $CH_2$ , NBD).  $^1H\{^{11}B\}$  NMR, partial,  $\delta$  ( $C_6D_6$ ): 3.26 (1H, dq, apparent coupling  $^3J_{HH}$  = 3.1 Hz,  $^1J_{RhH}$  = 13.1 Hz, BH).  $^{13}C\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): 152.64 [aza-C(7a)], 141.98 [aza-C(6)], 131.16 [aza-C(2)], 128.56 [aza-C(4)], 124.38 [aza-C(3a)], 114.17 [aza-C(5)], 101.19 [aza-C(3)], 59.00 (d,  $^3J_{RhC}$  = 6.5 Hz,  $CH=CH$ , NBD), 48.26 (d,  $^2J_{RhC}$  = 2.7 Hz,  $CH$ , NBD), 41.57 (d,  $^1J_{RhC}$  = 10.4 Hz,  $CH_2$ , NBD), 5.09 [br, B- $CH_3$  observed indirectly from HSQC].  $^{11}B$  NMR (96.2 MHz)  $\delta$  ( $C_6D_6$ ): -3.63 (d,  $^1J_{B-H}$  = 61.4 Hz, BH);  $^{11}B\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): -3.63 (s, hhw = 75 Hz). Elem. Anal.: Calcd for  $C_{23}H_{26}BN_4Rh$ : C 57.93; H 4.86; N 12.28; Found: C 56.76; H 5.14; N 11.92. IR (powder film): 2075  $cm^{-1}$  ( $\nu_{BH}$ ).

### Activation studies on $[Rh\{\kappa^3-N,N,H-B(Me)H(azaindoly)l_2\}(COD)]$ (**2**)

In a typical experimental procedure, a Young's NMR tube was charged with **2** (6.0 mg, 0.01 mmol). Degassed deuterated benzene was transferred into the tube to give a clear yellow solution (20 mM). The mixture was kept under partial vacuum and heated in an oil bath at 70 °C behind a blast shield for several days. The reaction progress was monitored by  $^1H$  and  $^{11}B$  NMR. After 21 d, 28% of a new complex was formed. The mixture was transferred into a Schlenk flask and the solvent removed. The residue was dissolved in a small amount of

degassed hexanes and passed through a plug of alumina (2  $\times$  6 cm) under a nitrogen atmosphere. The material was eluted with a mixture of hexanes:DCM (2:1) to give a mixture of the product **2a** (70% purity) and the starting complex in a ratio 7:3 (by  $^{11}B$  NMR). This mixture was recrystallised from a concentrated hexane solution at 4 °C to give a suitable crystalline sample for X-ray analysis. These were found to contain pure complex **2a**.  $^1H$  NMR  $\delta$  ( $C_6D_6$ ): 8.58 [1H, d,  $^3J_{HH}$  = 5.25 Hz, aza-CH(6)], 7.54 [1H, d,  $^3J_{HH}$  = 3.32 Hz, aza-CH(2)], 7.51 [1H, d,  $^3J_{HH}$  = 3.29 Hz, aza-CH(2')], 7.39 [1H, br d,  $^3J_{HH}$  = 5.18 Hz, aza-CH(6')], 7.36 [1H, dd,  $^3J_{HH}$  = 7.70 Hz,  $^4J_{HH}$  = 1.35 Hz, aza-CH(4)], 7.28 [1H, dd,  $^3J_{HH}$  = 7.70 Hz,  $^4J_{HH}$  = 1.25 Hz, aza-CH(4')], 6.47 [1H, dd,  $^3J_{HH}$  = 7.68 Hz,  $^3J_{HH}$  = 5.31 Hz, aza-CH(5)], 6.38 [1H, dd,  $^3J_{HH}$  = 7.54 Hz,  $^3J_{HH}$  = 5.20 Hz, aza-CH(5')], 6.34 [1H, d,  $^3J_{HH}$  = 3.28 Hz, aza-CH(3)], 6.31 [1H, d,  $^3J_{HH}$  = 3.28 Hz, aza-CH(3')], 5.02 [1H, m,  $CH=CH$  (allyl)], 4.69 [1H, m,  $CH=CH$  (allyl)], 4.25 [1H, t,  $^3J_{HH}$  = 7.78 Hz,  $CH=CH$  (allyl)], 2.63 [1H, t,  $^3J_{Rh-H}$  = 6.54 Hz,  $CH-Rh$  (cod)], 2.51 [1H, overlapping m,  $CH_2$  (cod)], 2.25 [1H, m,  $CH_2$  (cod)], 2.08 [1H, m,  $CH_2$  (cod)], 1.90 [1H, m,  $CH_2$  (cod)], 1.42 [1H, overlapping m,  $CH_2$  (cod)], 1.24 [1H, overlapping m,  $CH_2$  (cod)], 1.23 [1H, overlapping m,  $CH_2$  (cod)], 0.89 [1H, m,  $CH_2$  (cod)]. -2.29 [1H, br s. BH].  $^1H\{^{11}B\}$  NMR, partial,  $\delta$  ( $C_6D_6$ ): -2.29 (1H, d,  $^1J_{RhH}$  = 24.1 Hz, BH).  $^{13}C\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): 154.19 [aza-C(7a)], 153.30 [aza-C(7a')], 145.77 [aza-C(6)], 139.10 [aza-C(6')], 130.74 [aza-C(2')], 130.61 [aza-C(2)], 128.82 [aza-C(4)], 128.42 [aza-C(4')], 123.84 [aza-C(3a)], 123.20 [aza-C(3a')], 114.99 [aza-C(5')], 114.87 [aza-C(5)], 102.24 [aza-C(3)], 101.77 [aza-C(3')], 98.34 [=CH (cod), d,  $J_{RhC}$  = 5.28 Hz], 73.3 [=CH (cod), d,  $J_{RhC}$  = 14.84 Hz], 73.2 [=CH (cod), d,  $J_{RhC}$  = 9.71 Hz], 46.51 [ $CH_2$  (cod)], 46.30 [=CH (cod), d,  $J_{RhC}$  = 17.54 Hz], 43.28 [ $CH_2$  (cod)], 26.73 [ $CH_2$  (cod)], 26.14 [ $CH_2$  (cod)].  $^{11}B$ -NMR (96.2 MHz)  $\delta$  ( $C_6D_6$ ): -0.80 (d,  $^1J_{B-H}$  = 47 Hz, BH);  $^{11}B\{^1H\}$  NMR  $\delta$  ( $C_6D_6$ ): -0.80 (s, hhw = 69 Hz). IR (powder film): 2025  $cm^{-1}$  ( $\nu_{BH}$ ).

### Crystallography

X-ray diffraction experiments on  $Li(MeCN)_2[MeBai]$  and the complexes **1**, **2** and **3** were carried out at University of Bristol on a Bruker APEX II diffractometer using graphite monochromised Mo- $K_\alpha$  radiation ( $\lambda$  = 0.71073 Å). Single-crystal X-ray diffraction studies of complex **2a** were carried out at the UK National Crystallography Service at the University of Southampton.<sup>20</sup> Data collections for the ligand and complexes **1** - **3** were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated in SAINT [Bruker 2000, SAINT – Data reduction Software, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA] and absorption corrections applied using SADABS [Bruker 2001, SADABS Bruker AXS area detector scaling and absorption correction, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA]. The structures were solved by direct methods in ShelXS<sup>21</sup> and refined by least squares minimisation against  $F^2$  in ShelXL-2015<sup>22</sup> using Olex2.<sup>23</sup> In the case of **1** and **2**, the Squeeze routine within Platon<sup>24</sup> was used to remove the contribution from a small amount of disordered solvent that could not be sensibly modelled. For complex **2a**, the sample was mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with HF Varimax confocal mirrors and an AFC12

goniometer and HG Saturn 724+ detector. Again, the crystal was kept at  $T = 100(2)$  K during data collection. Data were collected and processed and empirical absorption corrections were carried out using CrysAlisPro<sup>25</sup>. The structure was solved by Intrinsic Phasing using the ShelXT structure solution program<sup>26</sup> and refined on  $F_o^2$  by full-matrix least squares refinement with version 2018/3, of ShelXL<sup>22</sup> as implemented in Olex2.<sup>23</sup> The hydrogen atom (H1) on boron in the ligand and all complexes were found in the difference map and its position was allowed to refine freely. Crystal structure and refinement data are given in Table S1 in the electronic supplementary information. Anisotropic parameters, bond lengths and (torsion) angles for these structures are available from the cif file which can be found in the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). The corresponding CCDC codes are 1847138 and 1847347 - 1847350.

## Conclusions

In summary, we have reported the synthesis of a new azaindole based scorpionate ligand, [MeBai]<sup>−</sup> the first to contain an alkyl substituent at the boron centre. This new derivative have been utilised to prepare rhodium and iridium complexes containing 1,5-cyclooctadiene and a rhodium complex containing 2,5-norbornadiene as co-ligands. Crystal structures have been obtained for all three complexes each of which confirm significant B–H–transition metal interactions. This is supported by solid state infrared spectroscopy. We have also confirmed that these interactions remain in the solution state as evidenced by detailed multinuclear spectroscopy data. The presence of the methyl group at boron does not appear to lead to migration of the hydride from boron to metal centre. In the series of group nine diene complexes containing the Tai, PhBai, MesBai, NaphthylBai and MeBai ligands there is only one of the 15 complexes which undergoes spontaneous hydride, [Rh(Tai)(NBD)]. Further investigations are necessary in order to understand the prerequisites for this hydride migration process. While there is no apparent migration of hydride in the reported complexes, we have demonstrated that [Rh(MeBai)(COD) **2**] undergoes an unusual transformation leading to the reduction of the COD ligand to form [Rh(III)( $\eta^1\eta^3$ -C<sub>8</sub>H<sub>12</sub>)(MeBai)]. Currently, the transformation is sluggish and does not proceed to completion. Although similar transformations have been observed at iridium centres, this is the first time it has been observed at a rhodium centre (in the absence of an external oxidant). Based on previous studies it is likely that this transformation involves a rhodium-hydride intermediate. We are currently exploring new systems where this transformation proceeds more readily to further understand how this occurs.

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## Notes and references

† The complex, [RhCl(COD<sup>Me</sup>)]<sub>2</sub> was prepared *via* a similar methodology as [RhCl(COD)]<sub>2</sub>. Details are provided in the experimental section.

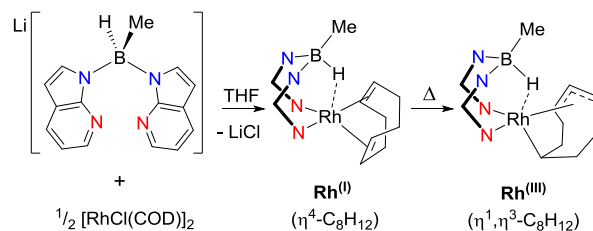
†† The BH signals in the <sup>1</sup>H{<sup>11</sup>B} NMR spectra were broad which made it difficult to measure these coupling constants to a high degree of accuracy, particularly in the case of complex **2**.

§ The shortest distance of the three structures is provided in the main text, the other two Rh–B distances are 2.944(3) and 2.957(3) Å.

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## Graphical Abstract



## Graphical Abstract Text

A new methyl substituted scorpionate ligand has been coordinated to group nine complexes. The reactivity of the complexes was explored.